

SANDIA NATIONAL LABORATORIES
CHEMICAL & DISPOSAL ROOM PROCESSES DEPARTMENT 6748
WASTE ISOLATION PILOT PLANT PROJECT

TOP-535

CALIBRATION, USE, AND MAINTENANCE OF pH METERS AND PROBES

Revision 0

Effective Date: 1/5/96

Author: John W. Kelly John W. Kelly 11/29/95
Print Signature Date

Technical W. Graham Yelton W. Graham Yelton 11/29/95
Reviewer: Print Signature Date

PI Approval: Hans W. Papenguth Hans W. Papenguth 11/30/95
Print Signature Date

QA Approval: Aldred L. Stevens Aldred L. Stevens 12/3/95
Print Signature Date

Records Peggy J. Warner Peggy J. Warner 12/4/95
Center Print Signature Date
Approval:

1.0 REVISION HISTORY

This document replaces TOP-6119-01 draft 2. The only purpose for this revision is to comply with SNLA-WIPP QA requirements.

2.0 PURPOSE

This procedure provides for the calibration operation, and maintenance of specific types of pH measurement instruments as part of the laboratory geochemistry research activities in support of the Waste Isolation Pilot Plant (WIPP) Project.

3.0 RESPONSIBILITIES

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure is responsible for implementing the requirements of this procedure.

The Project Scientist (PS), or designee, is responsible for performing the calibrations and measurements following the requirements of this procedure, documenting calibrations, and assuring that the latest revision of this document is followed.

4.0 SAFETY

This document does not address ES&H issues. Laboratory ES&H procedures are described in laboratory-specific SOPs in which the equipment is used and shall be adhered to.

5.0 CONTROLS

Controls are established by written procedures or instructions prepared in accordance with QAP 5.3, PREPARING, REVIEWING, AND APPROVING TECHNICAL OPERATING PROCEDURES, of the Sandia National Laboratories WIPP Quality Assurance Program. Procedures are issued in accordance with QAP 6.1, DOCUMENT CONTROL SYSTEM of the Sandia National Laboratories WIPP Quality Assurance Program.

6.0 SCOPE

This procedure is applicable only for the Model 720A pH meter, the Model EA 940 pH meter, the Model 960 Autochemistry System, and Ross Combination Electrodes, all made by Orion Research. This procedure applies to the calibration, operation, and maintenance of the aforementioned pH meters.

This document is not meant to substitute for the manufacturers instruction manuals for the pH meters and electrodes. The user is responsible for reading and understanding the appropriate manuals (see references).

In preparing this procedure, standardized, published methods were reviewed and incorporated when applicable. Specifically, EPA SW-846 (Chapter 6, Method 9040), Standard Methods for the Examination of Water and Wastewater (Method 4500-H⁺), and the 1993 Annual Book of ASTM Standards (Section 11, #D 1293-84) were reviewed.

6.1 SELECTION

The PI, or designee, will ensure that the pH meter and probe (electrode) are of the proper type, design, range, accuracy, and tolerance to accomplish their required function.

6.2 IDENTIFICATION

The pH meters are identified by manufacturer, model number, and serial number.

When not supplied with a serial number, the electrodes will each be assigned a permanent number that will be recorded in the laboratory notebook when that electrode is used.

6.3 STANDARDS

Calibration will be attained using commercially obtained pH standard buffer solutions that are traceable to NIST or other nationally recognized standards. The lot numbers and expiration dates of the standards used shall be recorded in the laboratory notebook.

The pH standard buffer solutions will not be used past the expiration date listed on the container by the manufacturer.

6.4 FREQUENCY

The instrument will be calibrated on the days it is used, prior to use. It will be recalibrated immediately if instrument irregularities are observed.

A performance test will performed immediately after calibration, and will include measurement of an appropriate pH standard buffer solution not used during calibration. If an occasional measurement is made, the meter will be tested just prior to use. If a set of measurements is made, the meter will be tested at the beginning and at the end of the set, as well as hourly during the set. If any test shows that the difference between the pH of the measurement and the known pH of the buffer is greater than 0.1 pH units, the meter shall be recalibrated.

6.5 PERFORMANCE TEST CRITERIA

Performance tests will be done by measuring the pH of an appropriate pH standard buffer solution(s).

If the difference between the pH of the measurement and the known pH of the buffer is greater than 0.1 pH units, the meter shall be recalibrated.

6.6 TEMPERATURE

Either an ATC (automatic temperature compensator) will be used, OR:

A calibrated thermometer shall be used to measure room temperature, and the samples and buffers shall be given sufficient time to equilibrate to this temperature. If the temperature of any solution is in doubt, or may have been changed by a mechanical device, such as a magnetic stirrer, its temperature will be measured and recorded. This temperature will be entered into the pH meter, and the temperature-corrected values of the pH buffers will be used.

6.7 ELECTRODE PREPARATION

The fill hole must be uncovered prior to use. The electrode must be upright, and the level of the electrode fill solution must be higher than that of the sample.

When electrode fill solution is added to an electrode, it should not be used for at least 4 hours.

7.0 CALIBRATION

The calibration procedure is identical for all three of the models listed in this TOP. The instrument calibrations are performed to the manufacturer instructions from the Orion Model EA 940 Instruction Manual. They are in the form of photocopies of the appropriate pages of this manual, attached as Appendix I.

The pH values of the buffer used must bracket the values of the samples to be measured. If the pH values of the samples exceed those of the standards, the meter must be recalibrated with appropriate buffers.

The slope must be between 92% and 102%.

If the pH meter and probe (electrode) cannot be calibrated, dispose of the pH standard buffer solution and recalibrate using fresh pH standard buffer solution. If the meter and probe still cannot be calibrated, change the electrode and recalibrate using fresh pH standard buffer solution. If the pH meter still cannot be satisfactorily calibrated, the meter will be taken out of service and either repaired or replaced.

8.0 PROCEDURE: pH MEASUREMENT

The electrode should be rinsed with deionized water, then gently blotted dry with a lint-free tissue prior to measurement.

Unless small sample size (20mL or less) makes it impractical, the following method will be adhered to prepare for sample analysis: Establish equilibrium between electrode and sample by stirring sample to insure homogeneity; stir gently to minimize carbon dioxide entrapment. For samples of low ionic strength, condition electrodes after cleaning by dipping them into a portion of the sample for at least 1 minute, then blot dry and immerse in a fresh portion of the same sample.

To initiate sample analysis, immerse the tip of the electrode in the sample. Wait for the reading to stabilize before recording. The stability criterion varies according to the requirements and conditions of the experiment and should be recorded in either the scientific notebook or the procedure for that experiment. The minimum acceptable equilibration time is 30 seconds.

9.0 MAINTENANCE

pH meters shall be stored so as to minimize their exposure to dusty, corrosive, or excessively humid atmospheres, temperatures outside the range of 0°-40°C, and mechanical shock or vibration.

The dispenser for autotitration system of the Orion 960 should be flushed with deionized water after use.

pH standard buffer solutions shall be stored in containers that do not alter the pH of the solutions, such as polyethylene or Teflon. The solutions must be protected from sunlight and stored at temperatures between 15°C and 30°C (as per manufacturer). Containers shall have lids or caps to prevent spillage, and to prevent evaporation.

Short term storage of probes (electrodes) shall be under moist conditions and at ambient temperature. Long term storage (one month or more) shall be under dry conditions, with the probes (electrodes) capped. See appendix II for details on care and cleaning of electrodes.

10.0 QA RECORDS

pH meter and probe (electrode) calibrations and performance test results will be recorded in the laboratory notebook in accordance with Sandia National Laboratories WIPP Quality Assurance Program Procedure 20-2, "PREPARING, REVIEWING, AND APPROVING SCIENTIFIC NOTEBOOKS".

11.0 REFERENCES

American Society for Testing and Materials, 1993. *Annual Book of ASTM Standards, Section 11: Water and Environmental Technology*, American Society for Testing and Materials, Philadelphia, PA

Environmental Protection Agency, 1986. *SW-846: Test Methods for Evaluating Solid Waste*, Office of Solid Waste and Emergency Response, Washington, DC.

Greenberg, A.E., L.S. Clesceri, A.D. Eaton, 1992. *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC

Orion Research Incorporated, 1987. *Model EA-940 Expandable Ionanalyzer Instruction Manual*, Orion Research Incorporated, Boston, MA

Orion Research Incorporated, 1988. *Orion 960 Autochemistry System Instruction Manual*, Orion Research Incorporated, Boston, MA

Orion Research Incorporated, 1990. *Ross pH Electrode Instruction Manual*, Orion Research Incorporated, Boston, MA

pH MEASUREMENT

General Information

1. To maintain memory, always leave EA 940 in the **STANDBY** mode when not in use, rather than disconnected from line power.
2. All buffers and samples should either be at the same temperature, or, automatic (ATC), or manual temperature compensation performed.
 - a. To use automatic temperature compensation, plug the ATC probe into the jacks labelled ATC on the rear panel, and place into buffer/sample along with the pH electrode. Make sure the electrode isopotential point was properly identified, see **CHANGE THE ELECTRODE ID?** section of **OPERATOR MENU**.
 - b. If no ATC probe is used, all buffers and samples should be at the same temperature or manual temperature compensation used. The default value, 25°C, or the last temperature manually set will be used for calculations. See **SET TEMPERATURE?** section of **OPERATOR MENU**.
3. Stir all buffers and samples with a magnetic stirrer while a measurement is being made.

NOTE: Some magnetic stirrers generate enough heat to change solution temperature. To avoid this, place a piece of cork, foam rubber, or other insulating material between stirrer and beaker.

Set Up

1. Prepare pH electrodes as directed in the corresponding electrode instruction manual.
2. Securely connect electrodes to either input 1 or 2.
 - a. For separate pH and reference electrodes the BNC connector slides straight on; then is rotated to lock into place. The reference pin-tip slides straight into the reference jack.
 - b. For combination electrodes the BNC connector slides straight on; then is rotated to lock into place. No pin-tip connector to the reference jack is required.
3. Press speed, then 2, to get to **OPERATOR MENU**.
4. Using yes and no keys, step through the **OPERATOR MENU** to check or change any method parameters, such as:
 - Electrode ID and isopotential point
 - Number of decimal places
 - pH limits
 - Timer
 - Print interval
 - Temperature
 - Time and date

Calibration and Measurement

Automatic calibration (autocal) allows quick and error-free calibration without requiring user to look up and manually enter pH values. The EA 940 automatically recognizes pH buffers 4.01, 7.00, and 10.01; and calibrates to the temperature corrected value. If the measured value is outside of the expected range, the buffer will not be accepted and "out of range" displayed. If this occurs, see **TROUBLESHOOTING**.

Manual calibration allows any pH buffer to be entered and used for calibration.

Either pH calibration sequence may be used for 1, 2, or 3 buffer calibrations. For best accuracy, choose 2 buffers that will bracket the expected sample pH and that are no more than 3 pH units apart.

Following is the sequence of messages displayed by the EA 940 when using a pH electrode. (Numbers used are for illustration only.)

| Display | Action |
|---|--|
| 1. OPERATOR MENU? 10:00 10-11-87 | Press no. (If data in operator menu needs to be checked or changed, press yes.) |
| 2. CALIBRATE 1:pH? 10:01 10-11-87 | Press yes. |
| 3. ENTER NUMBER OF BUFFERS (1-3) | Press 1, 2, or 3. Number of pH buffers chosen will be displayed for 2 seconds. |
| 4. DO AUTOMATIC CALIBRATION? | Press yes for autocal or no for manual. |
| 5. 1:pH ELECTRODE IN BUFFER 1? | Place electrode in first buffer and press yes. |
| 6. BUFFER 1 = 7.35 NOT READY | None required. Electrode response is unstable, wait for a stable reading. NOTE: EA 940's internal stability criteria may be overridden and current stability accepted for calibration by pressing yes. |
| 7. BUFFER 1 = 7.06 CAL AS 7.00? | Press yes if "cal as" value is correct value of your pH buffer. If performing a manual calibration, use numeric keys to change cal value if it is incorrect. Then press yes. |

If only one buffer is used for calibration, go to step 8a.

(Continued)

CONCENTRATION MEASUREMENTS

Calibration and Measurement (cont.)

If more than one buffer is used for calibration, repeat steps 5 through 7 for each additional buffer. Then go to step 8b.

| Display | Action |
|---|--|
| 8a. If 1 buffer was chosen: | |
| SLOPE = 100.0% IS THIS CORRECT? | Press yes if slope is correct. Use numeric keys to change slope if it is incorrect. Then press yes . If actual slope is unknown, enter 100% or perform a two point calibration. |
| 8b. If 2 or 3 buffers were chosen: | |
| SLOPE = 98.0% YES TO CONTINUE | Note electrode slope, then press yes to measure pH. |
| 9. MEASURE 1:pH? 10:03 10-11-87 | Place electrodes in sample and press yes . |
| 10. 1:pH = 6.77 10:04 READY 23.1°C | Record pH value when READY is indicated. The READY indicator is a verification of electrode stability. While measuring, the display may be stable before READY illuminates because the electrode signal is monitored over a period of time. The instrument criteria for monitoring READY is dependent on the display resolution selected. Choose the resolution appropriate for the analysis, and the EA 940 will automatically adjust the READY criteria. As many samples as desired may be analyzed without further operations. Press no to exit measure mode. (All calibration data will be stored in memory until that channel is recalibrated.) |

Calibration Adjustment

To adjust calibration for small changes due to electrode drift, press 2nd function, 9. This will allow a one buffer, manual calibration to be performed (steps 5 through 8a above).

DO NOT use cal adj if electrode slope or temperature have changed.

General Information

This information is for both **direct measurement** and **incremental techniques**.

1. A variety of techniques are available to measure concentration using ion-selective electrodes. The choice of technique will depend upon sample type, range of expected concentrations, and desired speed and accuracy.
2. Any concentration units (ppm, molarity, oz/gal...) may be used for calibration; result displayed will be in same units.
3. Allow all samples and standards to reach the same temperature before measurement, or use automatic temperature compensation if electrode isopotential point is known.

Automatic Temperature Compensation:

Ion-selective electrodes can be used with automatic temperature compensation, if the isopotential point of the electrode in use has been determined (check electrode instruction manual). Be sure that the isopotential point has been properly identified on EA 940. (See **CHANGE ELECTRODE ID?** section of **OPERATOR MENU**.)

Plug ATC probe into jacks labelled ATC on rear panel and place into standards and samples along with electrodes.

To Monitor Sample Temperature:

The automatic temperature compensation (ATC) probe may also be used to monitor temperature during ISE measurements.

The isopotential point must be set to the default value of 1.000. (This disables the automatic temperature compensation program but does not affect the temperature measurement capability.)

Plug ATC probe into jacks labelled ATC on rear panel, and place into standards and samples along with electrodes.

4. Stir all standards and samples with a magnetic stirrer while measurement is being made.

NOTE: Some magnetic stirrers generate enough heat to change solution temperature. To avoid this, place a piece of cork, foam rubber, or other insulating material between stirrer and beaker.

Direct Calibration Measurement

Direct measurement technique involves calibrating the EA 940 with one to five standards of known concentration. Unknown sample concentrations are then read directly from the display in the concentration units used for calibration.

Electrode Storage

To ensure a quick response and free-flowing liquid junction, the sensing element and reference junction must not be allowed to dry out.

Short-term Storage (up to one week)

Soak electrode in pH Electrode Storage Solution, Orion Cat. No. 910001. If ORION Storage Solution is not available, use about 200 ml pH 7 buffer to which about 1 gram KCl has been added, as a temporary substitute.

Long-term Storage

The reference chamber should be filled and the filling hole securely covered. Cover the sensing element and/or reference junction with its protective cap containing a few drops of storage solution. Before returning the electrode to use, prepare it as a new electrode.

Electrode Maintenance**Weekly**

1. Inspect the electrode for scratches, cracks, salt crystal build-up, or membrane/junction deposits.
2. Rinse off any salt build-up with distilled water, and remove any membrane/junction deposits as directed in the cleaning procedures below.
3. Drain the reference chamber, flush it with fresh ROSS Filling Solution, Orion Cat. No. 810007, and refill the chamber.

Cleaning Electrode

General - Soak in 0.1 M HCl or HNO₃ for half an hour, followed by soaking in storage solution for at least one hour.

Removal of Membrane/Junction Deposits

Protein - Soak in 1% pepsin in 0.1 M HCl, for 15 minutes.*

Inorganic - Soak in 0.1M tetrasodium EDTA solution for 15 minutes.*

Grease and Oil - Rinse with mild detergent or methanol solution.*

*After any of these cleaning procedures, drain and refill the reference chamber and soak the electrode in storage solution for at least one hour.